Spectroscopic Ellipsometry and Positron Annihilation Investigation of Sputtered HfO_2 Films

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Abstract

Hafnium oxide (HfO_2) films were prepared by pulsed sputtering method at different O_2/O_2+Ar ratio, deposition pressure, and sputtering power. Spectroscopic ellipsometry (SE) and positron annihilation spectroscopy (PAS) were used to investigate the influences of various deposition parameters on open volume defects in HfO_2 films. The results showed that low O_2/O_2+Ar ratio was critical to obtain the films with dense structure and low open volume defects. Meanwhile, the film density increased and the open volume defects decreased when the deposition pressure increasing. The film which deposited at high sputtering power showed a denser structure and lower open volume defects. Our results suggest that SE and PAS are effective techniques to study the optical and defect properties of HfO_2 and the results provide insights for the fabrication of high-quality HfO_2 thin films for optical application.

Keywords: HfO_2; Spectroscopic ellipsometry; positron annihilation spectroscopy; open volume defects

1. Introduction

Hafnium dioxide (HfO_2) has been used frequently as an alternative of SiO_2 dielectric layer in MOS devices [1-3] and optical coatings in many extreme environments [4-6]for its excellent properties, such as large band gap, high dielectric constant, good chemical and thermal stability, and high transparency from visible to infrared region. It is well known that both electrical and optical properties of HfO_2 films can be affected by many factors, including crystallography, microstructure, integral stoichiometry, binding states, morphology, contaminations, and defect density [7. For such reason, the films should be well evaluated before use.

A number of analytical techniques have been used to evaluate these factors. Spectroscopic

ellipsometry (SE) is one of the most fundamental and effective tools to study the optical properties of thin film. From SE data, the refractive index and thickness of the film can be easily derived. Considering the refractive index related to the properties of the film, SE measurement can obtain the densities, the compositions information and so on [8, 9].

Positron annihilation technique is a sensitive method to characterize the microsctructure of defects and the chemical environment around the position of positron annihilation in the solids. Doppler broadening spectroscopy (DBS) of slow positron beam is one specific analytical approach to study the surface of thinfilm materials [10, 11]. Uedono *et al.* had successfully applied this method to study the impact of TiN deposition on HfO_2 [12] and to characterize thin $HfSiO_x$ and $HfAlO_x$ films [11] and thin HfSiON films [13]. In DBS method, S and W parameters are usually used to characterize the information of positron annihilation.

In this paper, both SE and DBS of slow positron beam have been adopted, respectively to study the optical properties and the defects of the HfO_2 thin films which deposited by pulsed DC magnetron sputtering. The results show that low O_2/O_2+Ar ratio, high sputtering pressure and power can obtain dense and low defects films.

2. Experimental

HfO_2 films were deposited by magnetron reactive sputtering supplied with a pulsed power on n-type Si (100) substrates. The substrates were cleaned by Radio Corporation of America (RCA) method before loaded into the chamber. A high purity metallic hafnium plate (> 99.99%) with diameter of 90 mm was used as a target. The distance between the target and the substrate was kept 50 mm. Prior to the deposition, the chamber was pumped down to 2.0×10^{-3} Pa by a turbo pump and then high purity oxygen (O_2, > 99.999%) and argon (Ar, >99.999%) mixture gas with total flow rate of 30 sccm was introduced into the reaction chamber. Finally, seven HfO_2

samples were prepared at the different conditions. The sputtering parameters of the samples were listed on Table I. Of all the samples, the 2# was repeatedly used to compare with that deposited under the deferent O_2/O_2+Ar ratio, pressure and power.

In order to investigate the refractive indices of HfO_2 films, SE spectra were collected using a Horiba Jobin Yvon MM-16 Spectroscopic Ellipsometer in the range from 430 nm to 850 nm. The refractive index of the film was determined from SE data using Tauc-Lorentz model [14, 15] based on a four-layer stack structure (Si/SiO_2/HfO_2/50%HfO_2+50%void, the stack structure has been adopted by other researchers and proven to be effective[16, 17]). Doppler broadening spectra (DBS) of slow positron beam were measured using the slow positron beam line settled in Institute of High Energy Physics, China. Positron beam is generated by a ^{22}Na radiation source (50 mCi). The energy of positrons can be changed from 0.18 keV to 25.18 keV. The γ rays generated by positron annihilation were detected using a high-purity germanium detenter. Each spectrum of positron annihilation was collected with total counts of about 5×10^5. S parameter was defined as the ratio of the counts in the central region of the annihilation peak (510.56~511.44 keV) to total counts in the annihilation peak. W parameter was calculated via dividing the summed counts in the high energy regions (505.05~508.5 and 513.5~516.95 keV) by total counts in the annihilation peak. S parameter mainly reflects the positron annihilation with low momentum electrons, and W value represents the information of high momentum electrons. For example, a positron trapped in vacancy-type or open volume defects (such as nanovoids and vacancy clusters) reduces the recombination probability with the core electrons. Such status usually leads to higher S value and lower W parameter. The crystallinity of the samples was characterized by X-ray diffraction (XRD) operated with an X'pert Pro (Philips) X-

ray diffractometer with a monochromatic source of Cu Kα radiation (wavelength of 0.154066 nm) at a gazing angle of 1˚.

3. Results

The as-prepared samples are divided into three groups according to their preparation conditions, i.e. various O_2/ (O_2+Ar) ratio (denoted as R in the following), deposition pressure, and sputtering power. The influence of the sputtering conditions on the properties of the samples is shown and discussed as following.

Fig. 1 presents the refractive indices of the samples deposited under the various Rs (0.07, 0.26 and 0.59) as a function of the photonic energy. It can be seen that the refractive index decreases as R increases. The variation of the refractive index is generally caused by two factors: (a) the stoichiometric ratio, and (b) the density of the sample. The sample of near-stoichiometric often shows lower refractive index [18]. The low refractive index indicates that the oxidization of Hf atoms in the sample is enhanced. Additionally, the refractive index can also be used as an important indicator to evaluate the density of the HfO_2 sample [9]. The small refractive index implies low density of the sample. However, from the SE spectra, we cannot determine that either the stoichiometry or density is the main factor causing the change of refractive index. Therefore, which factor is the main factor should be further differentiated by positron annihilation.

The S parameters for HfO_2 samples deposited under R = 0.07, 0.26 and 0.59 as a function of incident positron energy are shown in Fig. 2. According to the feature of the S-E curve, we divide the curve into four parts. In the energy range of E < 0.68 keV, the S parameters mainly contributed by the positron annihilation from the surface. The second section is the range of

energy from 0.68 to 8.18 keV, which corresponding to mean implantation depth of the positron varies from 1.3 nm to 110 nm, calculated using the positron diffusion theory in solid. In this energy range, the tiny change of S parameter show that positron annihilated in a uniform region of film. It maybe assumed to the information of positron annihilation in HfO_2 films. As the energy of positron beam increased from 8.18 keV to 20.18 keV, the S parameter increased monotonously. In this range, the corresponding implantation depth of positrons is larger than 110 nm. The gradually increasing of S parameter mainly corresponds to the annihilation in the interface layer of the film and substrate. Such interface layer may be constituent of a mixture of hafnium silicate, hafnium silicide and silicon oxide [19-21]. In this region, the S value increases from the S value of HfO_2 to that of Si (about 0.5), which suggests the reduction of Hf content and the increase of Si content. The S value becomes a constant with value of 0.5 when the positron energy larger than 20.18 keV. It indicates that the positron annihilated in the Si substrate.

Compared a series of S curves (of which each curve represents the film deposited under a R ratio), in the platform of section two, the S value raise along with R increasing. In particular, the S value of HfO_2 film deposited at R of 0.07 is the closest one to that of the sintered HfO_2 (0.4328 ± 0.0005) [11]. Generally, the reduction of the annihilation between the positron and the electrons surrounding the O atom, as well as the annihilation of the positron in the high concentration of open volume defects will result in the rising of the S value [12, 22-24]. Positron may be sensitive to neutral or negative O??? vacancy and Hf vacancy, but not sensitive to positive charged O vacancy because of mutually exclusion. In HfO_2, the quantity of positive charged O vacancy is much more than that of the neutral and the negative. Combined with the SE results, we exclude that O vacancy is not reason for S value increasing.??? If O vacancy is the main factor to affect the S value, the larger S value indicates there are more O vacancies in the

film. But such results are inconsistent with previous SE analysis. Via above analysis, it is clarified that the decreasing of refractive index is attributed to decline of the film density in our experiments.

Open volume defect is another factor to affect the S value. If the positrons are trapped by open volume defects, it will produce higher S value. From the DBS results, the open volume defects increase clearly along with R increasing and the film deposited at R of 0.07 shows the lowest open volume defects. By analyzing both DBS and SE data, it can be seen that the bigger R obviously lead to larger open volume defects.

Fig. 3 shows the refractive indices of the samples deposited under the total pressure of 0.7, 1.0, and 4.0 Pa as a function of photonic energy. It can be seen that the refractive indices of the samples increase as the pressure increasing. And this result suggests that the density of the film remarkably increases with the increasing of the deposition pressure, namely open volume defects in the samples decrease. The refractive index of the film deposited at the pressure of 4.0 Pa can be estimated as of about 2.00 at the light wavelength of 632.8 nm, which is the closest one to that of the bulk HfO_2 (2.08) [25]. On the other hand, the refractive index can also be contributed by the component of metal Hf in the sample. But it is proven to be negligible by the following DBS results.

The S values of the HfO_2 samples deposited under the total sputtering pressure of 0.7, 1.0 and 4.0 Pa as a function of incident positron energy is shown in Fig. 4. It shows that the S parameters are not clear changed too at the uniform region of HfO_2 layer. Besides, it can be seen that the S value decreases along with pressure increasing. Combining with SE results, it can be concluded that the reduction of S value should mainly be due to the open volume defects decreasing, i.e., the open volume defects reduce as the pressure growing.

Fig. 5 shows the refractive indices of the samples deposited under different sputtering power (25, 45, and 100 W). It can be seen that the refractive index obviously increase as the sputtering power raising. Similar to the previous analysis, the increase of refractive index indicates that the density of the film increase. Under the sputtering power of 100 W, the refractive index of the film is up to 2.09 at the wavelength of 632.8 nm, which is extremely closed to that of the bulk HfO_2 (2.08). This suggests that the sample deposited at 100 W is more compact. On the other hand, the increase of metal Hf component in the sample may be also responsible for the enlargement of the refractive index. The latter reason is not dominant according to the following DBS analysis.

The S values of HfO_2 samples deposited under the sputtering power of 25, 45 and 100 W as a function of incident positron energy is shown in Fig. 6. Because the growth time of all samples was fixed as one hour, it can be found that the thickness of the film broadens as the sputtering power. And it is notably that the S value of the samples deposited under 100 W is 0.4736 as the positron energy increased to 25.18 keV, which is smaller than that of Si. This indicates that the positron has not implanted into the Si substrate. Moreover, the uniform region of HfO_2 layer in the spectra also shifts toward the high-energy as increasing sputtering power. In this uniform region of HfO_2 layer, the S value decreases as the sputtering power. The increase of S value can also be attributed to the higher O component and the less open volume at the higher power. However, the SE results do not show that the O component increases as power increasing. Thus, the increase of S value can be undoubtedly attributed to the reduction of open volume defects. Additionally, the S value of the sample deposited at 100 W can be estimated as of about 0.4296, which is similar to that of the sintered HfO_2 (0.4328). It is consistent with SE Data. Compared with other two samples, both S value and the refractive index of the film deposited at 100 W

changed significantly, indicating that the sample deposited at 100 W is very dense and has very little open volume defects.

4. Discussions

During the reactive sputtering, a lot of negative charged oxygen ions exist in the plasma because the O atoms are electronegative. At the action of the electric field, negative oxygen ions will bombard the surface of the sample [26]. As R increasing, the oxygen ion content in the plasma increases, as well as the bombardments. The enhanced bombardment may be responsible for the increase of open volume defects. From XRD Patterns of the HfO_2 films shown in Fig. 7(a), all the samples present monoclinic phase (JCPDF#65-1142). The average crystal sizes of the samples derived from the (110), (-111), (111) and (002) peaks of the XRD patterns using the Scherrer formula are 5.4, 5.0 and 4.5 nm, corresponding to the samples deposited under R=0.07, 0.26, and 0.59, respectively. In other word, that is the crystalline becomes better when R reduce. This result supports our conclusion got from SE and DBS.

Keeping the R, the amount of negative oxygen ions increase with pressure rising. However, at a high pressure, the mean free path of the ion in the plasma becomes shorter due to the more frequent collisions. It brings two effects. First, the growth rate decreases due to reduction of Ar ions energy [27]. The film deposited under low growth rate may gain better crystalline and less open volume defects. Another is that the more non-uniform surface may be induced by frequent bombardment of the ions under high pressure. The reduction of the open volume in the internal of HfO_2 film under high pressure can be attributed to low oxygen ions of injection depth for frequent collisions. It indicates that HfO_2 layer get less bombardment under high pressure, and less bombardment will result in the less open volume defects. Moreover, the sample will be heated to a high temperature by bombardment [28], which could bring better crystallization and

less open volume defects. It is supported by glancing angle XRD results. The XRD patterns of the samples deposited at the different pressure are shown in Fig. 7(b). The average grain sizes are calculated using same method and the values are 4.7, 5.0, 6.5 nm, corresponding to the samples deposited under pressure of 0.7, 1.0 and 4.0 Pa, respectively. It can be seen the crystallinity of the sample deposited at high pressure is better than that deposited at low pressure.

However, negative oxygen ions in the plasma will get large energy under high power. One hand, this will result in thickening of the film surface, and thick film surface will lead to more open volume defects than that of the internal of HfO_2 film. On another hand, the more bombardment will heat the samples obviously [28]. Like discussion at last section, more bombardment will get better crystalline and less open volume defects film. Moreover, the grain size could increase with the increasing thickness [29]. Similarly, it may result in the less open volume defects under higher power. Similar, it is supported the average grain sizes derived from XRD, which shown in Fig. 7(c). At this moment, the values of the average grain sizes are 4.4, 5.0, 5.7 nm corresponding to the film deposited at power of 25, 45 and 100 W, respectively. From calculated results, it can be concluded that the crystalline of the HfO_2 film is improved as the power get bigger.

5. Conclusions

In a summary, HfO_2 films had been prepared by the sputtering with a pulsed DC supply. Positron annihilation was proved to be an effective method to characterize HfO_2 films, especially open volume defects in the films. The low O_2/O_2+Ar ratio was found to obtain denser film with less open volume defects. Meanwhile, we can get same results from the film deposited under high pressure. Moreover, the density and open volume defects of HfO_2 film were obviously affected by the inward pulse power and the high power is helpful to deposit film with denser

and less open volume defects. Our results suggest that both SE and PAS are effective techniques to study the properties of HfO_2 thin film and the conclusions can guide the preparation of high-quality HfO_2 film vice versa.

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Tables caption:

Table I The deposited parameters of the HfO_2 samples.

Figure Captions

Fig. 1 The refractive indices of the HfO_2 samples deposited under R=0.07, 0.26, and 0.59. The work pressure and sputtering power were fixed at1.0 Pa and 45 W, respectively.

Fig. 2 The dependence of S parameter of the HfO_2 films deposited under R=0.07, 0.26 and 0.59 on the incident positron energy.

Fig. 3 The refractive indices of the HfO_2 samples deposited under the pressure of 0.7, 1.0, and 4.0 Pa. The oxygen ratio R and sputtering power were fixed at 0.26 and 45 W, respectively.

Fig. 4 The dependence of S parameter of the HfO_2 samples deposited under the pressure of 0.7, 1.0, and 4.0 Pa on the incident positron energy.

Fig. 5 The refractive indices of the HfO_2 samples deposited under the power of 25, 45, and 100 W. The oxygen ratio R and work pressure were fixed at 0.26 and 1.0 Pa, respectively.

Fig. 6 The dependence of S parameter of the HfO_2 samples deposited under the power of 25, 45 and 100 W on the incident positron energy.

Fig. 7 XRD patterns of the HfO_2 samples deposited at the different deposition condition: (a) R=0.07, 0.26 and 0.59; (b) the pressure of 0.7, 1.0, and 4.0 Pa; (c) the power of 25, 45 and 100 W.